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㉙ **Method for treating a potable water supply component made of a copper-based alloy.**

㉚ A method of treating a potable water supply component, for example a pipe, pipe coupling or tap body, made of a leaded copper-based alloy such as a brass or gun metal, in order to inhibit the leach out of lead from the alloy by potable water during service, comprises treating at least internal surfaces of the component with an aqueous solution of an acid that forms a substantially water insoluble compound with lead. The acid is preferably orthophosphoric acid.

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This invention relates to potable water supply components made of copper alloys, especially but not exclusively pipe fittings made of leaded brasses.

It is well known to make water pipe fittings, for example pipe couplings and valve and tap bodies, of brass or other copper based alloys such as gun metal. Normally, such alloys need to be free machinable so that, for example, requisite screw threads can readily be machined on the fittings. For that reason, it is well known to add a small quantity, typically from about 1 to 5 wt%, of lead during manufacture of the alloy.

Recently, however, concerns have been expressed, in the context of potable water plumbing systems, that lead might be leached out of such alloys during service, possibly giving rise to a health problem. The present invention seeks to mitigate this problem.

According to the present invention in its broadest aspect, there is provided a method of treating a potable water supply component made of a leaded copper-based alloy in order to inhibit the leach out of lead from the alloy by potable water during service, the method comprising treating at least internal surfaces of the component with an aqueous solution of an acid that forms a substantially water insoluble compound with lead.

Preferably, the acid is an oxy-acid of phosphorus, for example orthophosphoric acid, and the remainder of the body of this specification refers, for convenience, mainly to the use specifically of orthophosphoric acid. However, it is to be understood that alternative acids may, in principle, be used. In this connection, whilst we do not fully understand how the acid treatment functions, it is believed, without in any way limiting the scope of the invention, that the acid stabilizes or "passivates" lead at or near the internal surfaces of the treated component by causing the formation of a physically stable, adherent film of a substantially water insoluble simple or complex lead compound, for example a phosphate in the case where an oxy-acid of phosphorus, such as orthophosphoric acid, is used. In addition, the acid may act during the treatment actually to remove lead present at or near such surfaces.

By the expression "substantially water insoluble" used herein we mean preferably less than 0.01 g/L, and advantageously less than 0.001 g/L, at any temperature between 0 and 25°C.

The specific acid treatment and cleaning conditions mentioned hereinafter in relation to orthophosphoric acid generally apply also to the use of such other acids and, in any event, the optimum conditions may be determined by simple trial and experiment.

Preferably, the phosphoric acid is a technical or general purpose grade phosphoric acid comprising principally orthophosphoric acid, optionally together with relatively small amounts of other oxyacids of phosphorus such as pyrophosphoric acid. The phosphoric acid is preferably in the form of a dilute aqueous solution thereof, for example from 1 to 30% vol and preferably from 10 to 20% vol.

The phosphoric acid treatment may be carried out at substantially any ambient room temperature, although it is preferred to carry it out between 20 and 80°C, more preferably between 25 and 40°C, say around 35°C, for an extended period of time, say for between 30 and 120 minutes and typically between 60 and 90 minutes.

Also preferably, at least the internal surfaces of the component are cleaned, especially degreased, prior to the treatment with the acid. This may be effected using, for example, a mild detergent solution, preferably with simultaneous agitation, for example mechanical or ultrasonic agitation. Agitation, for example mechanical or ultrasonic agitation, may also be carried out during the phosphoric acid treatment step.

After the phosphoric acid treatment step, the component is preferably rinsed with water, and then allowed to dry or forcibly dried in a stream of hot air.

Whilst, of course, it is necessary to treat, in accordance with the invention, only those internal surfaces of the component that will come into contact with potable water during service, it is, where the treatment is carried out during manufacture of the component, expedient to immerse the whole component in, for example, a bath, a number of components preferably being treated simultaneously in a batch process.

Alternatively, however, the method of the invention may be performed in situ on a potable water supply installation. To that end, the acid solution would be introduced into the installation's pipework, following an optional cleaning/degreasing step, and allowed to remain in the pipework for, say, 1 to 2 hours whereafter the pipework would be flushed out with water and then put into, or back into, service.

In another aspect, the present invention provides a potable water supply component, for example a pipe or pipe fitting, made of a leaded copper-based alloy, which has been treated by the method defined above.

The following Examples illustrate the efficacy of the method of the invention.

Example 1

Twelve replicate, machined specimens of leaded dezincification-resistant brass (British Standard Institution's designation CZ132) were prepared in accordance with Annex A.4.1 of British Standard 7766:1994 entitled "Assessment of the potential for metallic materials to affect adversely the quality of water intended for human consumption" (previously embodied in the British Standard Institution's publication DD201:1991), the content

of which is incorporated herein by way of reference thereto. CZ132 brass contains 1.7-2.8wt% lead, 0.08 to 0.15wt% arsenic, 35 to 37wt% zinc, balance copper apart from up to 0.5wt% incidental impurities.

One of each of the replicate specimens was degreased in an ultrasonic tank using a 5% aqueous solution of a detergent (ex Canning) at 35°C. They were then immersed in 20% general purpose grade orthophosphoric acid (GPR grade from BDH) for 1½ hours at 35°C with occasional agitation. The specimens were then thoroughly rinsed with deionised water and dried in hot air.

The other of each of the replicate specimens was similarly treated, save that the orthophosphoric acid immersion step was omitted.

All twenty four specimens were then subjected to the extractive step set out in Annex A5 of BS7766:1994 and the extracts were analysed for lead using a carbon furnace atomic absorption spectrophotometer. The results obtained are shown in the following Table 1.

Table 1

Specimen No	Pb concentration Final Extract (ug/L) H ₃ PO ₄ treated	Pb concentration Final Extract (ug/L) Untreated
1	26.6	73.3
2	28.3	100.8
3	27.7	500.0
4	24.6	57.0
5	30.9	68.1
6	30.6	58.7
7	27.7	47.4
8	29.9	45.3
9	31.4	103.0
10	34.8	53.4
11	31.7	55.6
12	30.5	100.0

The "overall result", as defined in Annex A.7.1 of BS7766:1994, multiplied by 0.25 (see Section 3.1 of the Specification of BS7766:1994) for the orthophosphoric acid treated specimens was therefore 8.69 ug/L, i.e. well below the maximum permitted lead level of 50 ug/L, whereas the overall result x 0.25 for the untreated control specimens was 86.66 ug/L, i.e. well above the maximum permitted lead level.

Example 2

A number of replicate cast specimens of gun metal designated "LG1" in British Standard 1400:1985 were prepared as in Example 1, save that they were left unmachined, i.e. were in their as cast form. LG1 contains from 2.0 to 3.5 wt % tin, from 7.5 to 9.5 wt % zinc, from 4.0 to 6.0 wt % lead, from 0 to 2.0 wt % nickel, balance copper apart from incidental impurities.

The specimens were cleaned under the conditions shown in the following Table 2 and replicate ones were further treated with a 20 % vol aqueous solution of orthophosphoric acid under the conditions shown also in Table 2. The right hand column shows the "overall result" x 0.25 of the extractive step described in BS7766:1994. Whilst, compared with untreated CZ132 alloy, significantly less lead is leached out of untreated LG1, it is evident that phosphoric acid - treated LG1 shows a marked improvement.

Table 2

Alloy	Cleaning Step	H ₃ PO ₄ - Treatment Step	Overall Result X0.25 ug/L
LGI	5% Canning at 50°C + ultra-sonic agitation	-	17.0
LGI	5% Canning at 50°C + ultra-sonic agitation	20% vol at 50/80°C for 40 minutes + ultrasonic agitation	8.0

Claims

1. A method of treating a potable water supply component made of a leaded copper-based alloy in order to inhibit the leach out of lead from the alloy by potable water during service, the method comprising treating at least internal surfaces of the component with an aqueous solution of an acid that forms a substantially water insoluble compound with lead.

2. A method according to claim 1 wherein the acid is selected from one or more oxy-acids of phosphorus.

3. A method according to claim 2 wherein the acid comprises orthophosphoric acid.

4. A method according to any one of claims 1 to 3 wherein the acid has a concentration within the range of from 1 - 30% vol.

5. A method according to claim 4 wherein the acid has a concentration of about 10 - 20% vol.

6. A method according to any one of claims 1 to 5 which is carried out at a temperature between 20 and 80°C.

7. A method according to claim 6 which is carried out at a temperature between 25 and 40°C.

8. A method according to claim 7 which is carried out at a temperature of about 35°C.

9. A method according to any one of claims 1 to 8 wherein the acid treatment step is carried out for between 30 and 120 minutes.

10. A method according to claim 9 wherein the acid treatment step is carried out for between 60 and 90 minutes.

11. A method according to any one of claims 1 to 10 wherein, additionally, at least said internal surfaces of the component are cleaned with a cleaning solution prior to being treated with the acid.

12. A method according to claim 11 wherein the cleaning solution includes a detergent.

13. A method according to any one of claims 1 to 12 which is carried out during manufacture of the component.

14. A method according to any one of claims 1 to 12 which is carried out in situ in a potable water supply installation.

15. A method of treating a potable water supply component substantially as hereinbefore described in the Examples.

16 A potable water supply component, for example a pipe or pipe fitting, made of a leaded copper-based alloy which has been treated by a method as claimed in any one of claims 1 to 15.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 95 30 3197

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	MATERIALS PERFORMANCE, vol. 29, no. 8, 1 August 1990 HOUSTON (US), pages 45-49, XP 000175798 BOFFARDI B P 'MINIMIZATION OF LEAD CORROSION IN DRINKING WATER' * page 45, right column; figure 6 * * page 49 *	1-3, 16	C23C22/08 E03B7/09
Y	----- * page 49 *	4-8, 11-14	
Y	US-A-3 879 231 (WATANABE TAKASHI ET AL) 22 April 1975 * claims 1,2; examples 1-4; table 1 *	4-8, 11-14	
Y	US-A-4 089 707 (SHAFFER ROBERT J ET AL) 16 May 1978 * column 3; claims 1,2; table III *	4-8, 11-14	
P,A	DE-A-43 13 439 (IDEAL STANDARD) 27 October 1994 * column 1, line 15-42; claim 1 *		TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	GB-A-2 270 721 (DAIDO METAL CO) 23 March 1994		C23C C23F E03B
A	EP-A-0 171 043 (COLLARDIN GMBH GERHARD) 12 February 1986		
A	US-A-5 076 941 (BOFFARDI BENNETT P ET AL) 31 December 1991		
A	EP-A-0 510 989 (CALGON CORP) 28 October 1992		
A	EP-A-0 430 726 (UGINE ACIERS) 5 June 1991		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22 August 1995	Examiner Torfs, F
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>A : member of the same patent family, corresponding document</p>			

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